NOTES

A Mechanism for Polymer Melt or Solution Fracture

INTRODUCTION

In the extrusion of polymer solutions or melts through capillary dies, one usually observes with increasing extrusion rate the onset of a flow instability which is manifested as an irregular extrudate distortion. This instability is generally termed melt fracture, and is initially observed as an extrudate waviness or spiraling flow phenomenon which evolves at higher extrusion rates to a grossly distorted flow.

In recent years, a large number of theoretical and experimental studies of melt fracture have been published, and a variety of fracture mechanisms have been proposed. This literature has recently been critically reviewed by White,[1] and the reader is referred to his publication for background and bibliography. For our purposes, however, it is sufficient to note that the mechanisms previously proposed have led to criteria for the onset of fracture based on measurements in shearing flow. Here, we refer to the earliest criterion which suggested that fracture occurred at a critical value of the capillary wall shear stress (or shear rate), the later criterion of a critical value of the product of the capillary wall shear stress and the polymer molecular weight, and the more recent and well-received criterion which specifies a critical recoverable shear strain at the capillary wall. The key point to be noted, however, is that these onset criteria correlate melt fracture with measurements in the shearing flow within the capillary die.

It is the opinion of the present authors that correlation of the onset of melt fracture with measurements in shearing flow is inconsistent with experimental observation. The numerous direct visualization studies of velocity profiles and streaming birefringence patterns of melts entering and flowing within dies indicate quite conclusively that fracture is initiated at the capillary inlet, and the converging velocity field at this location is effectively an extensional flow. Fracture thus originates at a point where fluid elements are subjected primarily to extensional deformation, which strongly suggests that a consistent criterion for the onset of fracture must be related to fluid properties in extensional flow.

FRACTURE MECHANISM

The fracture mechanism proposed below is based on material behavior in extensional flow. This type of material deformation has received considerable attention in the literature from both a theoretical and experimental point of view. Of particular significance, however, the concept of a limiting extension rate in viscoelastic liquids was investigated in a recent communication by Denn and Marrucci.[2] Utilizing a convected Maxwell model with constant coefficients, these authors examined the theoretically predicted transient tensile stress growth following the onset of a constant extension rate in an initially unstressed fluid. Their results indicated that the well-known limiting condition

$$2\lambda\Gamma_c = 1 \tag{1}$$

where λ = characteristic material relaxation time and Γ_c = critical extension rate, did not determine the maximum possible extension rate as had previously been proposed. The extension rate defined by eq. (1) was found to represent a critical condition in the sense that for $\Gamma < \Gamma_c$, the time rate of increase of tensile stress was bounded and a finite steady-state stress level was attained; whereas for $\Gamma > \Gamma_c$, the tensile stress was found to increase exponentially with time and no limiting stress level was achieved. This behavior was attributed to the solid-like or elastic response of viscoelastic materials to rapid extensional deformation. In a later publication,[3] Gordon and Everage utilized a more realistic constitutive equation to examine this extensional phenomenon. Their results were in qualitative agreement with those of Denn and Marrucci. However, the critical extension rate was defined by

$$2\lambda\Gamma_c(1 - \epsilon) = 1 \tag{2}$$

where ϵ is a phenomenological constitutive parameter subject only to the condition

$$0 \leq \epsilon < 1. \tag{3}$$

From a qualitative point of view, the material behavior predicted in the analyses discussed above has been confirmed by the recent experimental observations of Meissner.[4] Using a novel tensile testing apparatus, Meissner found that low-density polyethylene ultimately attained a steady-state tensile stress level at low extension rates and exhibited an approximately exponential time rate of tensile stress growth at higher extension rates, leading to rupture of the fluid specimen.

The theoretical and experimental results briefly outlined above thus strongly suggest the existence of a critical value of the quantity $\lambda\Gamma$ for any polymeric material. An insight into the physical significance of this quantity may be obtained by examining the simple Maxwell model. For this model, the material relaxation time is given by

$$\lambda \equiv \frac{\eta_S}{G_S} = \frac{\eta_E}{G_E} \tag{4}$$

where η and G are the dashpot fluid viscosity and spring modulus, respectively, and the subscripts S and E refer to shearing and extensional deformation. The spring modulus, G_E, is given by

$$G_E = \frac{T}{\epsilon_R} = \frac{\eta_E\Gamma}{\epsilon_R} \tag{5}$$

where T is the tensile stress in the spring and ϵ_R is the recoverable extensional strain. Combining eqs. (4) and (5), one obtains

$$\lambda\Gamma = \epsilon_R \tag{6}$$

which indicates that the quantity $\lambda\Gamma$ may be identified with a recoverable extensional strain. Furthermore, the results discussed above may now be interpreted as indicating the existence of a critical value of this strain for any polymeric material. The proposed fracture mechanism follows immediately from this observation and may be stated as follows:

If the recoverable extensional strain in the capillary entrance region attains the critical value defined by eq. (1), the material at this location is unable to elastically deform with sufficient rapidity to reach a steady-state tensile stress level, and fracture may result. Thus, in the present theory we propose that melt fracture is a consequence of tensile failure of the material in extensional deformation.

DISCUSSION AND QUANTITATIVE EVALUATION

The fracture mechanism described above is similar in some respects to a mechanism recently proposed by Hürlimann and Knappe.[5] These investigators showed that the fracture criterion of Spencer and Dillon,[6] which specifies a critical value of the product of the wall shear stress and the polymer weight-averaged molecular weight, was equivalent to a critical capillary entrance pressure loss. The entrance pressure loss was then shown to be related to the maximum tensile stress in the melt at the capillary inlet, and fracture was hypothesized to be a result of tensile failure.

Although the ultimate failure mechanisms (i.e., a tensile failure) are identical in the two developments, the onset criteria differ significantly. In the present development, a critical recoverable extensional strain criterion is hypothesized, and the tensile stress increase in the capillary inlet region is considered to be a time-dependent stress growth resulting from the elastic response of a viscoelastic fluid to rapid extensional deformation. In the Hürlimann and Knappe analysis, on the other hand, a critical entrance pressure loss is proposed and correlated with a critical stress level.

It should also be noted that the tensile failure mechanism described above follows closely some ideas originally proposed by Tanner[7] in the development of a network rupture constitutive model. In this theory, Tanner proposed that a molecular catastrophy (rupture) occurs when a fluid element is strained to some critical degree, which is essentially equivalent to the fundamental hypothesis in the present fracture mechanism.

Quantitative evaluation of the fracture mechanism described above requires a calculation of the maximum extension rate in the entrance flow region at the onset of fracture. This is difficult since secondary (vortex) flows are generally observed in the capillary entrance region for most polymeric materials and lead to the characteristic "wine glass stem" shaped converging flow field. An approximate calculation may be obtained, however, utilizing the velocity field for laminar flow of an incompressible Newtonian fluid through a cone, which has been independently obtained by several investigators,[8,9,10] i.e.,

$$\nu_r = \frac{-3Q}{4\pi r^2} \cdot \left(\frac{\cos 2\theta - \cos 2\alpha}{(1 - \cos \alpha)^2(1 + 2 \cos \alpha)}\right) \cdot \tag{7}$$

where ν_r is the velocity component in the r direction, r is the radial distance from the cone apex at any angle θ, α is the cone semiangle, and Q is the volumetric flow rate. From eq. (7), the extension rate $d\nu_r/dr$ is given by

$$\frac{d\nu_r}{dr} = \frac{3Q}{2\pi r^3} \cdot \left(\frac{\cos 2\theta - \cos 2\alpha}{(1 - \cos \alpha)^2(1 + 2 \cos \alpha)}\right). \tag{8}$$

The maximum extension rate $(d\nu_r/dr)_{\max}$ occurs on the centerline ($\theta = 0$) at the entrance to the capillary. At this location, we have

$$r = \frac{D \cot \alpha}{2} \tag{9}$$

where D is the capillary diameter. Therefore,

$$\left(\frac{d\nu_r}{dr}\right)_{\max} = \frac{12Q}{\pi D^3 \cot^3 \alpha} \cdot \left(\frac{1 - \cos 2\alpha}{(1 - \cos \alpha)^2(1 + 2 \cos \alpha)}\right). \tag{10}$$

In terms of the capillary wall shear rate $\dot{\gamma}_w$, the maximum extension rate is given by

$$\left(\frac{d\nu_r}{dr}\right)_{\max} = \frac{3\dot{\gamma}_w}{8 \cot^3 \alpha} \cdot \left(\frac{1 - \cos 2\alpha}{(1 - \cos \alpha)^2(1 + 2 \cos \alpha)}\right). \tag{11}$$

It is immediately obvious on examination of this result that for the case of constant flow entry angle α, the present fracture mechanism implies the critical capillary wall shear rate criterion which has been observed experimentally.[1] Also, the experimentally observed diameter dependence of the critical volumetric flow rate at which fracture occurs, and the diameter independence of the critical wall shear rate, are consistent with eqs. (10) and (11).

The present mechanism can be quantitatively evaluated utilizing eq. (11) in conjunction with the experimental results of Ferrari,[11] who has determined the critical capillary wall shear rate for the onset of fracture of various melts in a series of capillaries of vary-

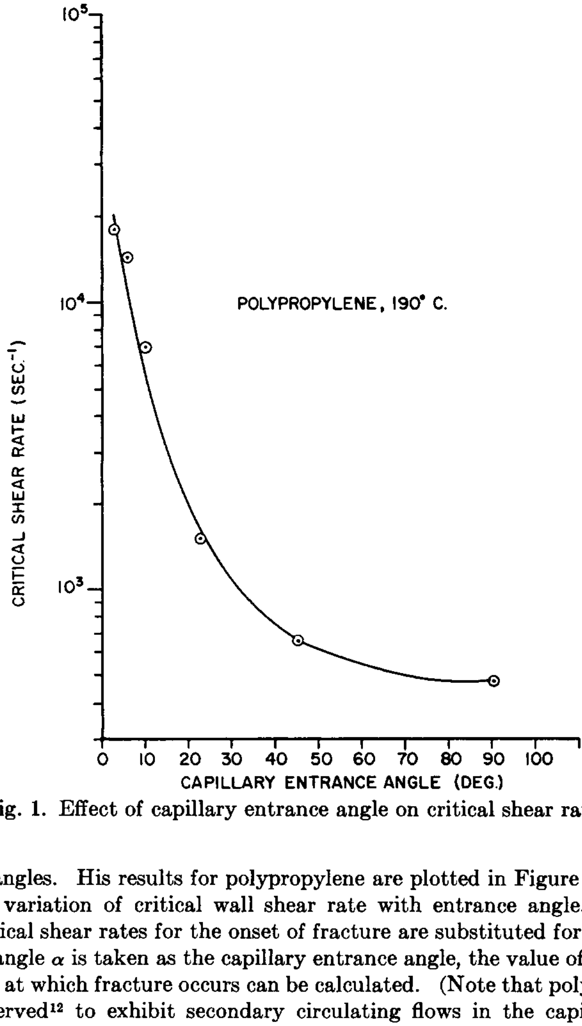

Fig. 1. Effect of capillary entrance angle on critical shear rate.

ing entrance angles. His results for polypropylene are plotted in Figure 1 and indicate a substantial variation of critical wall shear rate with entrance angle. However, if values for critical shear rates for the onset of fracture are substituted for $\dot{\gamma}_w$ in eq. (11), and the cone angle α is taken as the capillary entrance angle, the value of the maximum extension rate at which fracture occurs can be calculated. (Note that polypropylene has not been observed[12] to exhibit secondary circulating flows in the capillary entrance region, so that in this case the cone angle may be equated to the capillary entrance angle.) These results are tabulated in Table I and clearly indicate that while a 30-fold

TABLE I
Effect of Entrance Angle on Critical Shear Rate and Maximum Extension Rate

Cone semiangle α, degrees	Critical shear rate[a] $\dot{\gamma}_w$, sec^{-1}	Maximum extension rate $(dv_r/dr)_{max}$, sec^{-1}
3	20,000	1040
6	10,500	1113
10	5,800	1050
22.5	1,600	760
45	660	1195

[a] Values taken from smooth curve through experimental data.

variation in $\dot{\gamma}_w$ occurs, the maximum extension rate remains effectively constant. These results thus offer quantitative evidence in support of a fracture mechanism based on tensile failure in extensional flow.

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